

Theory of Thermal Conductivity of Zirconia Containing Rare Earth Solutes

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The factors controlling the thermal conductivity at ordinary and high temperatures of solid solutions of zirconia with rare earth oxides will be discussed. These are of the form $(\text{ZrO}_2) \cdot (\text{R}_2\text{O}_3)$, where R denotes a rare earth atom; the entire composition range being considered. Special attention is given to solutes of zirconia with gadolinium oxide (Gd_2O_3), recently studied by Wu *et al.* [1]. Solutions with oxides of other rare earths should behave similarly. The thermal conductivity of such solutions is reduced by point defects, which scatter phonons, as discussed earlier [2,3]. On the Zr-rich side these point defects are solute ions in the cation sublattice, and also oxygen vacancies needed to preserve charge neutrality. On the rare-earth rich side, the point defects are Zr ions in the cation sublattice, and also cation vacancies needed for charge neutrality. In the middle region around 50:50 cation concentration, the solution has the pyrochlore structure, $(\text{Zr}_2\text{R}_2\text{O}_7)$ for stoichiometry. For perfect order there would be no point defect scattering of phonons and the thermal conductivity should be intrinsic, *i.e.*, limited only by anharmonic phonon interactions, somewhat reduced by additional zone boundaries related to the additional Bragg scattering. However, thermal conductivity measurements for Gd, Nd and Sm pyrochlore phase samples show a much lower thermal conductivity, which indicates the presence of significant point defects, though less than in the surrounding compositions. The measurements agree with the supposition that there are no oxygen vacancies, but scattering of phonons by disorder in the cation sublattice. Since the pyrochlore phase was formed by quenching from the high-temperature cubic phase, the oxygen ions and vacancies reach their ordered pyrochlore structure rapidly, since oxygen diffuses rapidly in the cubic phase which contains oxygen vacancies. In the absence of cation vacancies, cation diffusion is much slower, and the disorder is maintained. It would be of interest if the presence of cation vacancies would speed up the attainment of order in the case of a slight excess of Gd, but still within the pyrochlore phase field.

[1] Jie Wu et al., J. Material Res., Dec. 2002, in print.

[2] P.G. Klemens, in "Thermal Conductivity 23" ed. by K.E. Wilks et al., Technomics Publishing Co., Lancaster PA, 1996, p. 209.

[3] P.G. Klemens and M. Gell, Material Science and Engineering A 245, 143 (1998).

[4] Jie Wu et al., J. American Ceramic Society 2002, in print.